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14. ABSTRACT

The support from the Office of Naval Research over the past 3 years has enabled us to make significant contributions to interest important to the Navy. Our research has focused in three areas. In the first area we have been advancing our understanding of aqueous surfaces as they pertain to understanding how water interacts with other media. We have been able to obtain detailed pictures of how water surfaces behave in the presence of high acid concentrations and adjacent to halocarbon surfaces. In the second area we have been examining the structure of molecular films that have important relevance to tribology. In these studies we have been working to understand how films assemble at surfaces and how to construct robust surfaces that can withstand chemical and physical pressures. The third thrust has been in developing molecular modeling capabilities to augment our experimental studies. These modeling capabilities have been extremely successful in giving us insights into how molecules behave at buried interfaces, particularly when in contact with other fluid media. As we move towards topics in environmental mediation in the coming funding period, the results of these current efforts will be invaluable.

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Final Progress Report
"Molecular Investigations of Interfacial Processes in Tribology"

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Overview and Goals of Proposed Research and Progress

Molecular surfaces and interfaces are ubiquitous in our world. Such interfaces are generally more fluid and flexible than their inorganic metallic or semiconductor counterparts, and also usually more reactive. Although recently there has been a growing interest in these more fluid interfaces comprised of aqueous solutions, organic solvents and films, macromolecules and polymers, what is known about their molecular properties and their mechanical and chemical behavior is dwarfed by what is unknown. Increasing our knowledge of the molecular behavior of such interfaces is of utmost importance to numerous issues of interest to the Navy and the Department of Defense (DoD). For example lubricants and molecular coatings of many forms and compositions are essential in creating an interfacial region that significantly reduces the friction between moving parts in everything from engines to computer drives. These molecular interfaces created by these organic films must withstand high temperatures, oxidation and often extreme pressures. Molecular interfaces also play a key role in the DoD's efforts in environmental remediation and prevention of contamination on defense sites. Chlorinated organic solvents are the most prevalent form of chemical contamination on these sites and are considered one of DoD's most serious environmental problems by the Strategic Environmental Research and Development Program (SERDP) of the DoD.[1] Understanding how chlorinated solvents and other non-aqueous phase liquids (NAPLs) interact with and permeate across boundary layers to spread into streams, aquifers and soils is key to developing remediation strategies to ameliorate past problems and prevent future hazards. Developing such strategies is not an easy task give the lack of information currently available about interfacial interactions between chlorinated solvents and aqueous solutions and soils.

The studies are aimed at using our extensive expertise in measuring and modeling behavior at molecular interfaces to assist the Navy in two key areas: tribology and environmental remediation. Our goal in these studies is to provide fundamental insights into molecular bonding, structure and reactivity that control the behavior of these interfaces in technologically important applications. The experimental studies will employ vibrational sum frequency spectroscopy (VSFS), a unique surface specific tool for *in-situ* measurements of molecular structure that is ideally suited for our goals. Molecular modeling studies will be conducted in conjunction with the experimental work. In the area of tribology we will continue our *in-situ* spectroscopic investigations of surfaces under stress. The behavior of confined liquids under the effects of pressure and wear, and the nature of chemistry that occurs under such extreme conditions, will be studied.

Our second area of focus is in environmental remediation and sustainability. These studies involve spectroscopic examination of the molecular properties of interfaces consisting of NAPLs in contact with aqueous solutions of different compositions of ions, acids, oxidants and heavy metals. Aliphatic chlorinated hydrocarbons (CAHs) will be the main class of NAPLs to be examined. These studies will be a combination of experiment and theory and build on some recent results in our laboratory that we initiated with the previous grant. The fluid interface between two immiscible liquids is a largely unexplored area of science from a molecular perspective but is receiving growing attention due to its importance to many environmental remediation efforts. The issues our studies will address lie at the heart of many environmentally important questions including the interaction of halocarbons with ground water, oil remediation, and the extraction and dechlorination of CAHs

B. Progress Towards the Research Goals

We have made progress in three areas since funding of this grant in March 2004:

(1) Molecular Dynamics Simulations of Liquid Surfaces:

Molecular structure and bonding interactions at the vapor-water interface of varying $H_2O/HOD/D_2O$ composition have been calculated using molecular dynamics simulations. From these simulations a surface vibrational sum frequency (VSF) spectrum of the OH stretch region has been generated and compared with experimental VSF results of similar isotopic mixtures. The peak frequency of the uncoupled, solvated OH stretch mode determined from the computational spectrum of the vapor-HOD interface shows excellent agreement with these experimental results. With the addition of H_2O, the calculations performed in this work provide information as to how various OH stretch modes at the vapor-water interface are impacted by the coupling effects that are induced by hydrogen bonding to adjacent OH oscillators. The results of these calculations demonstrate the frequency shifting, spectral broadening, and changes in transition strength exhibited by the OH stretch modes of interfacial water species that occur with increased intermolecular and intramolecular coupling, providing an improved understanding of the different types of water species present at the vapor- water interface that have been difficult to assign in previous VSF experimental studies.

(2) Monomer Exchange Dynamics of Monolayers at Salt Surfaces

The adsorption, desorption and equilibrium monomer exchange processes of sodium dodecanoate at the fluorite(CaF_2)/water interface have been studied. For the first time, we use in-situ vibrational sum-frequency spectroscopy (VSFS) to gain insights into the mechanism and kinetics of monolayer self-assembly at the solid-liquid interface. By exploiting the non-linear optical response of the adsorbate, the temporal correlation of headgroup adsorption and alignment of the surfactant's alkyl chain was monitored. Because of the unique surface specificity of VSFS, changes in the interfacial water structure were also tracked experimentally. The spectra clearly reveal that the structure of

interfacial water molecules is severely disturbed at the start of the adsorption process. With the formation of a well-ordered adsorbate layer, it is partially reestablished, however, the molecular orientation and state of coordination is significantly altered. Even at very low surfactant concentrations, overcharging of the mineral surface (i.e., the adsorption of adsorbates past the point of electrostatic equilibrium) was observed. This points out the importance of effects other than electrostatic interactions and it is proposed that cooperative effects of both water structure and surfactant hemi-micelle formation at the interface are key factors. The present study also investigates desorption kinetics of partially and fully established monolayers and a statistical model for data analysis is proposed. Additional experiments were performed in the presence of electrolytes and showed that uni- and divalent anions affect the non-equilibrium kinetics of self-assembled monolayers in strikingly different ways.

(3) Molecular Dynamics Calculations of Water/Halocarbon Interfaces

The upsurge of interest in the nature of water adjacent to hydrophobic liquids is due in part to the growing appreciation for its unique characteristics for supporting chemical synthesis, nanoparticle assembly, oil remediation, and a host of other chemical separation processes. The important characteristics of these interfaces that lend themselves to these applications—molecular orientation, polarity, interfacial charge and electric fields—all stem from the disruption of the bulk water hydrogen bonding network. Water molecules seem to adapt to hydrophobic neighbors by rearranging themselves to maximize available hydrogen-bonding opportunities and minimize unfavorable dipole interactions. Using equilibrium molecular dynamics simulations, we have discovered that this adaptation follows trends associated with the molecular properties of the hydrophobic liquid neighbor. Our studies reveal that the degree of water structuring in the immediate vicinity of the oil-water junction is highest when the hydrophobic phase is the least polar.